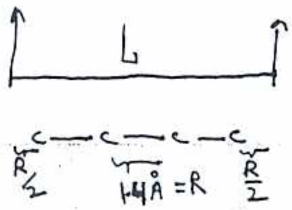
Chem. 1410
Sept. 17, 2007

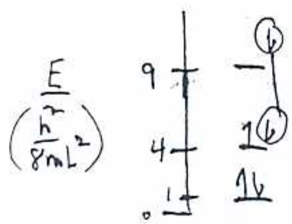
FEM for ...

Butadiene:

$\cong$



$L = 4R = 5.6\ \text{Å}$



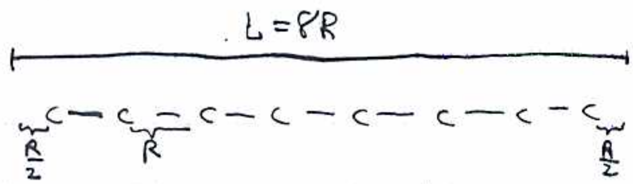
$$h\nu_{abs} = \Delta E = \boxed{\overset{37.6\,eV}{\frac{h^2}{8m_e(1\text{Å})^2}}}\ \frac{1}{[L(\text{Å})]^2}\left(3^2-2^2\right) = 5.99\ eV \times \frac{8.06\ E3\ cm^{-1}}{eV} = \overset{FEM}{\boxed{4.83E4\ cm^{-1}}}$$

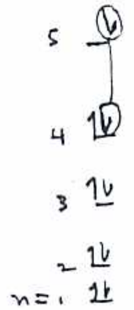
Note: $$\frac{h^2}{8m_e(1\text{Å})^2} = \frac{(6.625E{-27}\ erg\text{-}sec)^2}{8(9.1E{-28}\ gm)(1E{-8}\ cm)^2} = 6.03E{-11}\ erg \times \frac{6.24E11}{erg} = 37.6\ eV$$

NB: Exptl. result is $\boxed{4.61E4\ cm^{-1}}$

Tetraene:

$\cong$

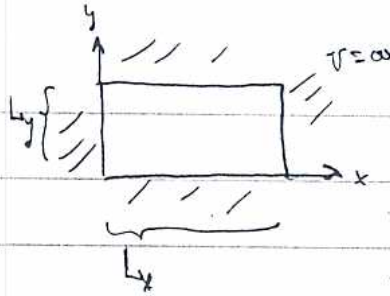




Now $$h\nu_{abs} = (37.6\ eV)\ \frac{1}{(8\times1.4)^2}\ (25-16) = 2.7\ eV = \boxed{2.17\ E4\ cm^{-1}} \Rightarrow \lambda = 4{,}633\ \text{Å}$$

Absorbs in blue ⇒
orange color

II) Particle in a 2-d (infinite box):



General Schröd. Eq. for motion in 2-d:

$$\Big[\underbrace{-\frac{\hbar^2}{2m}\Big(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\Big)+\underbrace{V(x,y)}_{\text{pot. energy}}}\Big]\psi(x,y)=E\,\psi(x,y)$$

For P. in B: (i) $V(x,y)=0$ inside Box

(ii) $V(x,y)=\infty$ outside box $\Rightarrow$ ψ must vanish at box edges (and outside)

(iii) try: $\psi_{jk}(x,y) = \sin(j\pi x/L_x)\sin(k\pi y/L_y)$

don't worry about normalization yet

Substitute: $$-\frac{\hbar^2}{2m}\Big(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\Big)\Big\{\sin\Big(\frac{j\pi x}{L_x}\Big)\sin(k\pi y/L_y)\Big\} = \overbrace{-\frac{\hbar^2}{2m}\Big[-\Big(\frac{j\pi}{L_x}\Big)^2-\Big(\frac{k\pi}{L_y}\Big)^2\Big]}^{E_{jk}}\Big\{\sin\Big(\frac{j\pi x}{L_x}\Big)\sin\Big(\frac{k\pi y}{L_y}\Big)\Big\}$$

It works!

Thus,

$$E_{jk}=\frac{\hbar^2\pi^2}{2m}\Big[\frac{j^2}{L_x^2}+\frac{k^2}{L_y^2}\Big] \qquad j=1,2,\dots;\ k=1,2,3,\dots$$

Normalize ψ_{jk} s.t. $\int_{-\infty}^{\infty}dx\int_{-\infty}^{\infty}dy\,|\psi_{jk}(x,y)|^2=1$ $\Rightarrow$ Normalized $\psi_{jk}(x,y)=\begin{cases}\sqrt{\frac{2}{L_x}}\sqrt{\frac{2}{L_y}}\sin\Big(\frac{j\pi x}{L_x}\Big)\sin\Big(\frac{k\pi y}{L_y}\Big) & \underline{\text{inside box}}\\ 0, & \underline{\text{outside box}}\end{cases}$

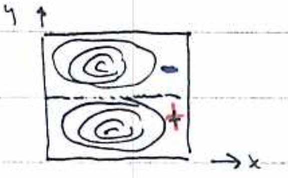
Features: (i) Interesting [nodal] patterns; cf. Fig. 12.7

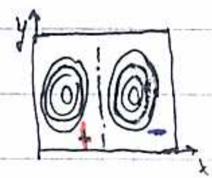
(ii) Degeneracies, when $L_x=L_y=L$

Consider, e.g. $j=1, k=2 \Rightarrow E_{12} = \frac{\hbar^2\pi^2}{2mL^2}(1+4)$; vs. $E_{21} = \frac{\hbar^2\pi^2}{2mL^2}(4+1)$; So: $E_{12} = E_{21}$

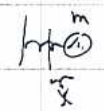
Eigenfnctns. ψ_{12}, ψ_{21} are topologically equivalent but distinct [due to differing orientation in space].

ψ_{12}





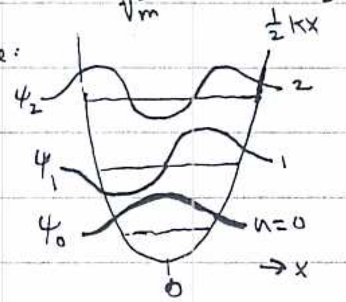
ψ_{21}

(III) Harmonic Oscillator:  $V(x) = \frac{1}{2}kx^2$; Schröd. Eq: $\left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2\right]\psi_n(x) = E_n\psi_n(x)$

Only for energies $E_n = (n+\frac{1}{2})\hbar\omega$; $n = 0, 1, 2, \ldots$ do acceptable ψ_n's exist [$\leftarrow |\psi| \to 0$ at $\pm\infty = x$]

$\sqrt{\frac{k}{m}}$

These eigenfnctns. look like:



Explicit expression for ψ_n:

$$\psi_n(x) = c_n H_n(y)\, e^{-y^2/2} \quad ; \quad y \equiv \sqrt{\frac{m\omega}{\hbar}}\, x \quad ; \quad c_n = \frac{1}{\sqrt{2^n n!}}\left[\frac{m\omega}{\pi\hbar}\right]^{\frac{1}{4}}$$

and

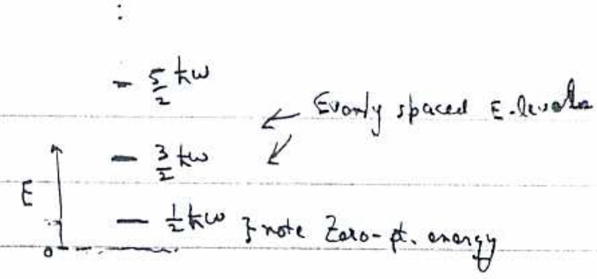
$H_n(y) = n^{th}$ Hermite polynomial; $H_0(y) = 1$

$H_1(y) = 2y$

$H_2(y) = 4y^2 - 2$

$H_3(y) = 8y^3 - 12y$

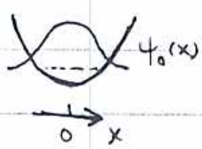
Properties of the H.O.: (a) evenly spaced E levels



(b) eigenfnctns. as sketched above

(c) Norm, expectation values ...

Ex., n=0



$$1 = N_0^2 \underbrace{\int_{-\infty}^{\infty} dx\, e^{-m\omega x^2/\hbar}}_{\sqrt{\frac{\pi\hbar}{m\omega}}} \Rightarrow N_0 = \left[\frac{m\omega}{\pi\hbar}\right]^{\frac{1}{4}} \checkmark$$

Note: $\int_{-\infty}^{\infty} dx\, e^{-Ax^2} = \sqrt{\frac{\pi}{A}}$

How about: $\langle x \rangle_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} dx\, x\, e^{-m\omega x^2/\hbar} = 0$

$$\langle x^2 \rangle_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{2}} \underbrace{\int_{-\infty}^{\infty} dx\, x^2 e^{-m\omega x^2/\hbar}}_{\frac{1}{2}\sqrt{\pi}\left(\frac{\hbar}{m\omega}\right)^{3/2}} = \frac{1}{2}\frac{\hbar}{m\omega}$$

Note $\frac{\partial}{\partial A}\int_{-\infty}^{\infty} dx\, e^{-Ax^2} = -\int_{-\infty}^{\infty} dx\, x^2 e^{-Ax^2}$

$$\langle p \rangle_0 = \sqrt{\frac{m\omega}{\pi\hbar}} \int_{-\infty}^{\infty} dx\, e^{-m\omega x^2/2\hbar} \underbrace{\frac{\hbar}{i}\frac{\partial}{\partial x} e^{-m\omega x^2/2\hbar}}_{-\frac{m\omega}{\hbar} x\, e^{-m\omega x^2/2\hbar}} = 0$$

$$\langle p^2 \rangle = \sqrt{\frac{m\omega}{\pi\hbar}} \int_{-\infty}^{\infty} dx\, e^{-m\omega x^2/2\hbar}\left(-\hbar^2\frac{\partial^2}{\partial x^2}\right) e^{-m\omega x^2/2\hbar}$$

$$= -\hbar^2\sqrt{\frac{m\omega}{\pi\hbar}} \int_{-\infty}^{\infty} dx\, e^{-m\omega x^2/2\hbar} \underbrace{\frac{\partial}{\partial x}\left[-x e^{-m\omega x^2/2\hbar}\right]}_{\left[-e^{-m\omega x^2/2\hbar} + \frac{m\omega}{\hbar}x^2 e^{-m\omega x^2/2\hbar}\right]} \frac{m\omega}{\hbar} = \hbar m\omega - \hbar^2\left(\frac{m\omega}{\hbar}\right)^2 \underbrace{\frac{\hbar}{2m\omega}}_{\langle x^2\rangle_0}$$

$$= \boxed{\frac{1}{2}\hbar m\omega}$$

Example: Vibrations of a Diatomic (+ Infrared Spectra →)

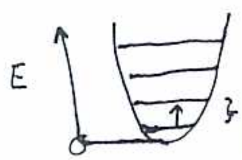
H.O. as a model of diatomic vibration: 

; $\mu \equiv \frac{m_1 m_2}{m_1 + m_2}$

Note classical Eq. for nonrotating diatom vibration $\mu \ddot{R} = -k(R - R_e) \Rightarrow \omega = 2\pi\nu = \sqrt{\frac{k}{\mu}}$

equilibrium position

Corresponding quantized vib E levels are: $\hbar\omega(n+\frac{1}{2})$, $n = 0, 1, 2 \ldots$



lowest energy photon that can be absorbed $= \hbar\omega \equiv$ "fundamental absorption frequency" } usually in infrared region of spectrum

Ex: for $^{75}Br\,^{19}F$, infrared spectrum consists of 1 intense line at 380 cm^{-1}. What is force constant?

$$\nu = \frac{c}{\lambda} = (380\,\text{cm}^{-1})(3E10\ \text{cm/sec}) = 1.14 \times 10^{13}\ \text{hz} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \Rightarrow \boxed{k\ (N/m)} = [(2\pi)(1.14 \times 10^{13})]^2 \cdot \overbrace{\frac{(75)(19)}{(75+19)}}^{15.16}\ \text{amu} \times \frac{1\,g}{6.02E23\ \text{amu}} \times \frac{kg}{1000\,g}$$

$$= \boxed{129\ N/m}\ \text{(typical)}$$